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STABILIZATION OF POLYMORPHIC PHASES IN OXIDES. POLYMORPHIC TRANSITIONS

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The polymorphic transitions in oxides, which are controlled by diffusion proceeding through a vacancy mechanism are considered. A certain ratio between the oxygen and cation vacancies is required to provide for the neutrality of the total electric current arising in ion movement. Since oxides usually have an excess of oxygen vacancies at high temperatures, a further increase in the content of oxygen vacancies through the introduction of respective additives delays diffusion, hampers the polymorphic transition, and stabilizes the phase. Introduction of additives which increase the concentration of cation vacancies, on the contrary, accelerates diffusion and facilitates the polymorphic transition.

The polymorphic transitions which occur in oxides, for instance, Al_2O_3, SiO_2, $2CaO \cdot SiO_2$, and ZrO_2, have a profound impact on the materials based on these oxides [1, 2]. Substantial rearrangement of the structure can take place in polymorphic transitions which are referred to as first-kind transitions. They are accompanied by significant alterations in the solid phase volume, involve mass transfer and because of that possess considerable inertia. Very rapid heating or cooling (quenching) can produce metastable phases in temperature regions in which these phases are not expected to exist. Some transitions require only very slight atomic displacement, for example, the transitions at the Curie point in ferroelectrics. They are called second-kind transitions.

In order to control polymorphic transitions, additives acting as stabilizers or destabilizers of the respective phase are widely used. There are various hypotheses for the effect of the additives on the polymorphic transition: variations in surface tension, different solubility of different phases, as solid solutions are formed, etc. [1]. The present paper discusses the stabilization and destabilization aspects in the context of the origin of cation and oxygen vacancies in formation of solid solutions. The purpose of the present study is to consider the effect of oxygen vacancies on the diffusion processes in polymorphic transitions in oxides in the context of synergism. The synergistic approach is the most general and provides for understanding of the phenomenon is essence [3 – 5]. The vacancies are regarded as the elements of a substructure which contains objects below 1 μm in size [6].

A polymorphic transition is an example of a phenomenon when a system in the form of a crystal lattice dissipates the energy flow fed into the system and creates dissipative structures. A substructure of atomic size dissipates the supplied thermal or mechanical energy by rearranging the relative positions of the atoms (ions) in the unit cell. Ceramics technology usually involves thermal energy.

Each separate atom in the crystal upon receiving thermal energy tends to transfer it to the neighboring structural element, primarily, to the neighboring atoms. It can be done most efficiently when there are many neighboring atoms and all directions toward them are equivalent, i.e., the chemical bonds are not directed. This can be observed in ionic crystals with a highly symmetric crystallographic structure, such as the cubic structure. In the case of all-round heating, the energy is dissipated not only on transferring heat to the neighboring atoms, but on increasing the length of the chemical bonds and the vibration amplitude as well. In highly symmetric crystals with highly ionic chemical bonds, such dissipation does not generate a need for changing the structure, and the system remains stable.

In crystals with a greater share of covalent chemical bonds and low symmetry, dissipation of the energy received by an atoms is hampered. The received energy has to be dissipated primarily along strongly directed (compared to ionic) bonds. Such bonds can have a very high transmitting capacity in phonons, i.e., exhibit high thermal conductivity, as is the case in diamond. The capability of strongly directed covalent bonds to increase the bond length and vibration amplitude on receiving energy is restricted. When the capacity of these bonds for dissipating energy to the neighbouring atoms is exhausted, the system is forced to convert to another structure. The new structure makes it possible to dissipate the supplied energy with higher efficiency and in fact is itself a dissipative structure. Efficient energy dissipation is facilitated by an increase in the number of the neighboring atoms

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and a decrease in the directivity of the chemical bonds, i.e., increased symmetry of the crystallographic structure. As a consequence, the high-temperature phases usually have a higher symmetry, in the limit, cubic symmetry.

In first-kind polymorphic transitions, the origin of new phase nucleations and growth of the new phase in the solid body are often controlled by diffusion processes. If diffusion occurs through a vacancy mechanism, the cation and anion mass flows have to be coordinated in such a way that the total electric current is equal to zero. The mass transfer is determined by the vacancy flow in the cation and anion sublattices [7]:

$$J_i = C_i M_i F_i,$$

where J_i is the vacancy flow in sublattice i; C_i is the concentration of vacancies in sublattice i; M_i is the mobility of the vacancies; F_i is the diffusion motive force.

The presence of both cation and anion (oxygen) vacancies is necessary for effective diffusion mass transfer in oxides contributing to the polymorphic transition, and the ratio of these vacancies should be close to the stoichiometric ratio between the cations and the anions in the oxide crystal corrected according to their mobility and motive force. In the contrary case, diffusion will be limited by the concentration of vacancies whose flow is below the level required to provide for a zero value of the total electric current. In this case the electric balance is disturbed. The system then delays diffusion through the appearance of an electric field oriented to hamper diffusion flow. Such phenomena are usually called polarization phenomena.

The maximum concentration of the cation and oxygen vacancies with their optimum ratio should facilitate the polymorphic transition. The vacancies are distinguished as thermal vacancies whose concentration depends only on the temperature and impurity vacancies depending on the concentration of impurities and additives [7]. Within the range of technological temperatures, the process is usually controlled by the vacancies arising due to the presence of impurities or modifying additives [8].

In most oxides the concentration of oxygen vacancies increases at high temperatures due to the higher volatility of the oxygen anion, as compared to the metal cation [9]. This process depends on the size of the crystals: it intensifies in highly disperse and finely crystalline ceramics. The cation and anion vacancies are related through Schottky equilibrium, i.e., the system will limit an increase in the oxygen vacancy content at the expense of a decrease in cation vacancies. Impurities, additives, the gas medium composition, and the presence of tensile and compressive stress fields in the crystal have a pronounced effect on the concentration of cation and anion vacancies. In order to accelerate diffusion carried out through the vacancy mechanism which is more common in oxides, it is usually necessary to introduce certain additives to polycrystalline materials, which increases the concentration of cation vacancies [9]. In complex oxides, one

ought to increase primarily the concentration of the slowest diffusing cations [10].

Nucleation of the seeds of a new polymorphic phase most often occurs on the surface of the phase boundary of the liquid or gas medium or another solid phase. This process is often controlled by the diffusion rate. It has to originate on the most energy-saturated sites of the surface with the highest chemical potential, known as active centers. The chemical bonds between the atoms in an active center area are weakened and can be broken and rearranged into a new structure, i.e., a new phase seed is formed. It is possible to delay this stage by lowering the energy of such centers, for example, through adsorption or chemisorption of the respective impurity atoms in these areas. It is important to prevent the adsorbed atoms from joining the atoms of the main phase, the impurity atoms, and vacancies and forming associates and seeds of a phase with a structure similar to the structure of the new polymorphic phase, i.e., to prevent them acting as crystal seeds.

The growth of the new phase nuclei is a diffusion process. It can occur directly in the solid phase or via the liquid phase. In the latter case, the defects have an impact on the dissolution rate of the previous polymorphic phase. If the dissolution process occurs in the diffusion region, the effect of the defects is leveled by the properties of the liquid diffusion layer. At high temperatures, most heterophase processes with participation of the liquid phase occur in the diffusion region, since in these conditions, the slowest determining stage is usually not the chemical reaction velocity, but the rate of diffusion through the diffusion layer. In this case, the vacancy concentration in the solid body does not have a determining effect on the polymorphic transition rate.

If growth of nuclei takes place in the solid phase, the concentration of vacancies and their mobility have a determining effect on the polymorphic transformation rate. The widely used method of stabilizing or destabilizing polymorphic phases with additives is based on the above fact. The additives and the main phase form solid solutions and change the concentration of oxygen and cation vacancies, as compared to the Schottky equilibrium in the absence of additives.

Thus, not only the concentration of vacancies in the cation and anion sublattices but their rate as well appear to have a determining effect on polymorphic transitions. A deviation from the vacancy concentration ratio ensuring that the total electric current in mass transfer will be equal to zero is expected to delay the polymorphic transitions.

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